ω-ETHOXYCARBONYL-, ω,ω-BIS(ETHOXYCARBONYL)- AND ω-(ETHOXYCARBONYL)-ω-CYANOALKYLTRIALKOXYSILANES

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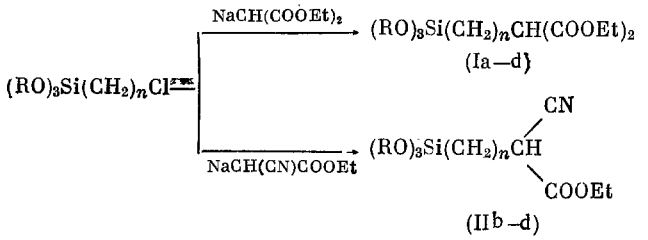
UDC 542.91:547.1'128

Organosilicon compounds containing an $Si(CH_2)_nCOOR$ group hold interest in the preparation of polymers and biologically active derivatives [1-5].

A convenient method for the synthesis of organyl(alkoxycarbonyl)alkylsilanes is the reaction of organyl(haloalkyl)silanes with sodium derivatives of C–H acids [4, 6-9]. However, compounds of this type containing three alkoxy groups at the silicon atom have not been reported.

We are the first to report the preparation of ω-(ethoxycarbonyl)alkyltrialkoxysilanes (I) and (II) in 16-48% yield.



$n = 1$, R = Me (a); $n = 1$, R = Et (b) $n = 3$, R = Me (c); $n = 3$, R = Et (d)

The (triethoxysilyl)alkylation of sodium ethyl cyanoacetate gives bis[(triethoxysilyl)-alkyl]cyanoacetates $[(EtO)_3Si(CH_2)_n]_2C(CN)CO_2Et$ (n = 1 (III) and n = 3 (IV)) in addition to the monosubstitution products (IIb) and (IId).

Due to the reversibility of the Claisen reaction [10], the ethyl ester of β-(triethoxysilyl)propionic acid was formed in 19-24% yield from sodium ethyl cyanoacetate and (chloromethyl)triethoxysilane.

$$(EtO)_3SiCH_2Cl + NaCH(COOEt)C(O)Me \xrightarrow{EtOH} (EtO)_3Si(CH_2)_2COOEt + MeCOOEt + NaCl \quad (V)$$

In contrast to organylalkoxy(haloalkyl)silanes [6], this reaction proceeds even in the case of excess (chloromethyl)triethoxysilane.

EXPERIMENTAL

The IR spectra of (I)-(V) were taken neat on a Specord 75-IR spectrophotometer.

[2,2-Bis(ethoxycarbonyl)ethyl]trimethoxysilane (Ia). A solution of MeONa in 90 ml methanol prepared using 8.6 g (0.37 g-atom) sodium was added dropwise over 1 h to a solution of 64 g (0.37 mole) $ClCH_2Si(OMe)_3$ and 60 g (0.37 mole) diethyl malonate in 100 ml monoglyme. The mixture was heated at reflux for 20 h and filtered. Methanol and monoglyme were distilled from the filtrate and the residue was fractionated in vacuum to yield 20 g (19%) (Ia). IR spectrum (ν, cm^{-1}): 1730 and 1750 (C=O).

[2,2-Bis(ethoxycarbonyl)ethyl]triethoxysilane (Ib). Analogously, 50 g (0.23 mole) $ClCH_2Si(OEt)_3$, 37.6 g (0.23 mole) diethyl malonate, 150 ml ethanol and 5.4 g (0.23 g-atom) sodium gave 24.6 g (31%) (Ib). IR spectrum (ν, cm^{-1}): 1740 and 1760 (C=O).

[4,4-Bis(ethoxycarbonyl)butyl]trimethoxysilane (Ic). Analogously, 60 g (0.030 mole) $Cl(CH_2)_3Si(OMe)_3$, 48.4 g (0.30 mole) diethyl malonate, 6.9 g (0.30 g-atom) and 90 ml methanol gave 34.3 g (35.5%) (Ic). IR spectrum (ν, cm^{-1}): 1740 (C=O).

Institute of Organic Chemistry, Siberian Division, Academy of Sciences of the USSR, Irkutsk. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 693-695, March, 1986. Original article submitted June 19, 1985.

 0568-5230/86/3503-0634$12.50

TABLE 1. ω-(Ethoxycarbonyl)alkyltrialkoxysilanes $(RO)_3Si(CH_2)_nCR'R''COOEt$

Compound	R	R′	R″	n	bp, °C (p, mm Hg)	d_4^{20}	n_D^{20}	Chemical formula	Found/Calculated, %			
									C	H	N	Si
(Ia)	Me	COOEt	H	1	99–101 (0,5)	1,1069	1,4255	$C_{11}H_{22}O_7Si_1$	44,65 / 44,88	7,31 / 7,53	–	9,89 / 9,54
(Ib)	Et	COOEt	H	1	113,5–114 (1,5)	1,0367	1,4220	$C_{14}H_{28}O_7Si_1$	49,88 / 49,97	8,20 / 8,39	–	7,71 / 8,35
(Ic)	Me	COOEt	H	3	119,5–120 (0,5)	1,0772	1,4316	$C_{13}H_{26}O_7Si_1$	48,39 / 48,42	7,82 / 8,13	–	8,67 / 8,71
(Id)	Et	COOEt	H	3	144 (2)	1,0208	1,4272	$C_{16}H_{32}O_7Si_1$	52,59 / 52,72	8,74 / 8,85	–	7,11 / 7,71
(IIb)	Et	CN	H	1	124–125,5 (1,5)	1,0377	1,4245	$C_{12}H_{23}N_1O_5Si_1$	50,27 / 49,80	7,96 / 8,01	4,77 / 4,84	9,85 / 9,70
(IId)	Et	CN	H	3	131,5–132 (1,5)	1,0098	1,4305	$C_{14}H_{27}N_1O_5Si_1$	52,67 / 52,97	8,48 / 8,57	4,37 / 4,41	8,48 / 8,85
(III)	Et	CN	$(EtO)_3SiCH_2$	1	162–164 (1,5)	1,0501	1,4325	$C_{19}H_{39}N_1O_8Si_2$	48,48 / 49,01	8,23 / 8,44	3,28 / 3,01	12,44 / 12,06
(IV)	Et	CN	$(EtO)_3Si(CH_2)_3$	3	179–181 (1)	1,0088	1,4363	$C_{23}H_{47}N_1O_8Si_2$	53,39 / 52,94	8,67 / 9,08	2,88 / 2,68	10,94 / 10,77
(V)	Et	H	H	1	85–86 (2)	0,9925	1,4130	$C_{11}H_{24}O_5Si_1$	49,88 / 48,97	8,68 / 9,15	–	10,57 / 10,62

[4,4-Bis(ethoxycarbonyl)butyl]triethoxysilane (Id). Analogously, 33.2 g (0.21 mole) diethyl malonate, 50 g (0.21 mole) $Cl(CH_2)_3Si(OEt)_3$, 4.8 g (0.21 g-atom) sodium and 200 ml ethanol gave 36.5 g (48%) (Id). IR spectrum (ν, cm^{-1}): 1740 (C=O).

[2-(Ethoxycarbonyl)-2-cyanoethyl]triethoxysilane (IIb) and Ethyl Bis(triethoxysilylmethyl)-cyanoacetate (III). Analogously, 72.3 g (0.35 mole) $ClCH_2Si(OEt)_3$, 40 g (0.35 mole) ethyl cyanoacetate, 8.1 g (0.35 g-atom) sodium and 120 ml ethanol gave 16.8 g (16.5%) (IIb) and 18 g (35%) (III). IR spectrum (ν, cm^{-1}): (IIb): 1725 (C=O), 2235 (C≡N); (III): 1725 (C=O), 2200 and 2225 (C≡N). Carrying out this reaction with an equimolar amount of ethanol in 70 ml diethylcarbitol at 120°C gave 34.6% (IIb) and 36.2% (III).

[4-(Ethoxycarbonyl-4-cyanobutyl]triethoxysilane (IId) and Ethyl Bis(triethoxysilylpropyl)-cyanoacetate (IV). Analogously, 13.7 g (0.12 mole) ethyl cyanoacetate, 29.4 g (0.12 mole) $Cl(CH_2)_2Si(OEt)_3$, 2.8 g (0.12 g-atom) sodium and 60 ml ethanol gave 13.4 g of a mixture of (IId) and (IV), bp 132-305°C (1.5 mm). Fractionation gave 8 g (20.7%) (IId) and 5 g (25.8%) (IV). IR spectrum (ν, cm^{-1}): (IId): 1735 (C=O), 2245 (C≡N); (IV): 1745 (C=O), 2245 (C≡N).

[2-(Ethoxycarbonyl)ethyl]triethoxylsilane (V). a) Analogously, 30.6 g (0.23 mole) ethyl acetoacetate, 50 g (0.23 mole) $ClCH_2Si(OEt)_3$, 5.4 g (0.23 g-atom) sodium and 100 ml ethanol gave 11.8 g (19.1%) (V). IR spectrum (ν, cm^{-1}): 1740 (C=O).

b) A mixture of 41 g (0.32 mole) ethyl acetoacetate and 7.2 g (0.32 g-atom) sodium in 70 ml diethyl carbitol was heated until the sodium was completely dissolved and then $ClCH_2Si(OEt)_3$ was added dropwise and heated for 25 h at 110-130°C. The mixture was filtered to remove the precipitate and distilled in vacuum to give 19.9 g (24%) (V).

The physical constants and elemental analysis data for (I)-(V) are given in Table 1.

CONCLUSIONS

(Chloroalkyl)trialkoxysilanes react with sodium ethyl malonate and sodium ethyl cyanoacetate to give the corresponding ω-(ethoxycarbonyl)alkyltrialkoxysilanes, while the reaction of sodium ethyl acetoacetate with (chloromethyl)triethoxysilane gives ethyl (triethoxysilyl)-propionate.

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